

## PATENT ABSTRACTS OF JAPAN

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(21)Application number : **07-075152**

(71)Applicant : **NIPPON OIL CO LTD**

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### (54) SEPARATOR FOR ALKALINE BATTERY AND ALKALINE BATTERY

(57)Abstract:

PURPOSE: To enhance stability, and particularly lengthen the cycle service life of a secondary battery by forming an alkaline battery having a separator.

CONSTITUTION: A separator for an alkaline battery which is substantially formed of a cross linked body obtained by cross-linking polyvinyl alcohol under the existence of a cross-linking agent and on which the cross-linking agent is sodium tetraboric acid and/or its hydrate and whose cross-linked body is formed independently or integrally with a mesh-like structure body and is characterized by having a sheet-like shape or the like and an alkaline battery having these, are provided. A separator is excellent in electrolyte resistance, dendrite resistance and an electrolyte keeping characteristic, and is useful since ion conductivity is excellent.

### LEGAL STATUS

[Date of request for examination]

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the alkaline cell which consists of an alkali primary cell and an alkali rechargeable battery equipped with the separator for alkaline cells, and this separator.

[0002]

[Description of the Prior Art] Conventionally, alkaline cells, such as a nickel-zinc cell, a nickel-cadmium battery, and a zinc-manganese cell, are equipped with the separator, in order to prevent the short circuit of a positive electrode and a negative electrode. Generally as a charge of separator material, the nonwoven fabric which consists of fiber, such as a polyamide, polypropylene, and a polysulfone, is used.

[0003] The aforementioned polyamide system nonwoven fabric has bad hot alkali resistance, since degradation by cutting of a chain takes place, while in use, a dendrite occurs and there is a trouble that a positive electrode and a negative electrode will short-circuit. Although excelled in alkali resistance, since the aforementioned polypropylene system nonwoven fabric is a hydrophobic property, its electrolytic-solution retentivity is bad. Therefore, if charge-and-discharge efficiency is bad and makes thickness thin, a leakage current will arise, and there is a trouble of it becoming impossible to use it as a cell. Although the electrolytic-solution retentivity of the aforementioned polysulfone system nonwoven fabric is good as compared with a polypropylene system nonwoven fabric, when thickness is made thin like a polypropylene system nonwoven fabric, a leakage current arises and there is a trouble of it becoming impossible to use it. further -- these nonwoven fabrics -- each -- fine -- since it has the hole, the actual condition cannot fully suppress a dendrite and especially generating of this dendrite is a critical defect in a zinc system alkaline cell

[0004] On the other hand, the laminating of the polyvinyl alcohol is carried out on a nonwoven fabric like a polypropylene nonwoven fabric, and the proposal (JP,3-1457,A) of creating a separator is made. However, there is a problem of the dendrite-proof nature of polyvinyl alcohol being inadequate, and causing degradation in the electrolytic solution.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is excellent in electrolytic-solution-proof nature, dendrite-proof nature, electrolytic-solution retentivity, etc., and is to offer the ion conductivity good separator for alkaline cells. Another purpose of this invention is to offer an alkaline cell with the high stability equipped with the separator which has the property which was excellent the account of before.

[0006]

[Means for Solving the Problem] According to this invention, it becomes substantial from the polyvinyl alcohol bridge formation object which constructed the bridge over the bottom of existence of a cross linking agent, and obtained polyvinyl alcohol, and the separator for alkaline cells characterized by these cross linking agents being sodium tetraborate and/or a sodium-tetraborate hydrate is offered. Moreover, according to this invention, it becomes substantial from the sheet-like object of the polyvinyl alcohol bridge formation object which constructed the bridge over the bottom of existence of a cross linking agent, and obtained polyvinyl alcohol, and the separator for alkaline cells which these cross linking agents are sodium tetraborate and/or a sodium-tetraborate hydrate, and is characterized by uniting the aforementioned sheet-like object with a network-structure object is offered. Furthermore by this invention, the alkaline cell equipped with these separators for alkaline cells is offered.

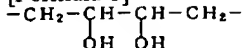
[0007] Hereafter, this invention is further explained to a detail. The separator for alkaline cells of this invention consists of substantially polyvinyl alcohol bridge formation objects which constructed the bridge in polyvinyl alcohol considering sodium tetraborate and/or the sodium-tetraborate hydrate as a cross linking agent.

[0008] although especially the polyvinyl alcohol used by this invention is not limited -- average degree of polymerization 200-10000 -- it is preferably desirable 300-6000, and that it is 500-3000 still more preferably Since there is an inclination for the viscosity of polyvinyl alcohol solution to rise and for creation of a separator to become difficult when average degree of polymerization is less than 200, there is a possibility that dendrite-proof nature may fall and 10000 is exceeded, it is not desirable. Moreover, the degree of saponification has a desirable thing high as much as possible, and it is usually preferably desirable [ the degree ] that it is 97% or more still more preferably 90% or more 80% or more. The hydrophilic property of polyvinyl alcohol falls [ the degree of saponification / a low ], and the electrolytic-solution retentivity of a separator becomes bad.

[0009] Although the aforementioned polyvinyl alcohol usually consists of 1 and 3-diol combination, 1 and 2-diol combination shown in the formula-ization 1 other than this combination as different-species combination may be contained.

[0010]

[Formula 1]



[0011] This combination tends to receive oxidization cleavage in alkali as compared with 1 and 3-diol combination, and causes separator degradation. therefore, there are as much as possible few 1 of the polyvinyl alcohol used by this invention and 2-diol joint contents -- desirable -- usually -- less than [ 5.0 mol % ] -- it is preferably desirable less than [ 2.0 mol % ] and that it is less than [ 0.5 mol % ] still more preferably Measurement of this 1 and 2-diol joint content can be performed using <sup>13</sup>C-NMR.

[0012] The cross linking agents used by this invention are sodium tetraborate, sodium-tetraborate hydrates, or such mixture. Although especially a sodium-tetraborate hydrate is not limited, ten hydrates (borax), five hydrates, etc. are usually used.

[0013] the compounding ratio at the time of making the aforementioned polyvinyl alcohol construct a bridge by the aforementioned cross linking agent -- 100 mol % of monomers of polyvinyl alcohol -- receiving -- 0.05-5.0 mol % of cross linking agents -- it is preferably desirable that it is [ 0.15-3.0 mol % ] % still more preferably 0.10-4.0-mol% Since there is a possibility that ion conductivity may fall when the loadings of a cross linking agent are less than [ 0.05 mol % ], there is a possibility that dendrite-proof nature may fall and 5.0-mol % is exceeded, it is not desirable.

[0014] Although especially the crosslinking reaction for preparing the aforementioned polyvinyl alcohol bridge formation object is not limited, it is carried out by the method of sinking sodium-tetraborate solution into the polyvinyl alcohol film prepared beforehand, the method of trickling sodium-tetraborate solution into polyvinyl alcohol solution, etc. the account of before -- although especially polyvinyl alcohol thickness is not limited in the case of the method of sinking sodium-tetraborate solution into the polyvinyl alcohol film prepared beforehand, it is usually preferably desirable that it is 30-80 micrometers still more preferably 20-100 micrometers 10-200 micrometers Moreover, although it is not limited especially with [ the sodium-tetraborate solution concentration used in case it is made to sink in ] saturated concentration [ below ], it is usually preferably desirable concentration ] 0.1 to 5.0% of the weight that it is 0.5 - 5.0 % of the weight still more preferably 0.01 to 5.0% of the weight. As for the temperature at the time of sinking in, it is desirable that it is usually 10-90 degrees C, and is 20-80 degrees C preferably. As for sinking-in time, it is usually preferably desirable that it is for [ 10 minutes ] - 50 hours still more preferably for for 5 minutes to 120 hours for for 1 minute to 240 hours.

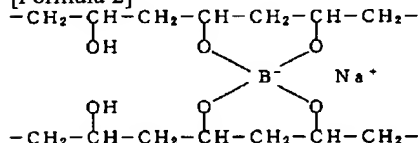
[0015] Although the polyvinyl alcohol solution concentration used for crosslinking reaction can be suitably adjusted according to the average degree of polymerization of polyvinyl alcohol in the case of the method of trickling sodium-tetraborate solution into the aforementioned polyvinyl alcohol solution, it is usually preferably desirable that it is 0.2 - 3.0 % of the weight still more preferably 0.1 to 5.0% of the weight 0.05 to 10% of the weight. Although it is not limited especially with [ sodium-tetraborate solution concentration ] saturated concentration [ below ], it is usually preferably desirable [ concentration ] that it is 0.5 - 2.0 % of the weight still more preferably 0.1 to 3.0% of the weight 0.01 to 5.0% of the weight.

[0016] When the aforementioned sodium-tetraborate solution is dropped at polyvinyl alcohol solution, it can carry out usually heating polyvinyl alcohol solution. Although heating temperature will not be limited especially if a polyvinyl alcohol bridge formation object is the temperature which presents a fluidity, it is desirable that it is 60-90 degrees C.

[0017] Although especially the structure of cross linkage of polyvinyl alcohol and a cross linking agent is not limited, it is usually JIJORU type bridge formation between molecules, and can illustrate the structure of cross linkage usually shown by the formula-ization 2 in model.

[0018]

[Formula 2]



[0019] Especially the grade of bridge formation of a bridge formation object may not be limited, and any of partial bridge formation or whole bridge formation are sufficient as it. When making it specifically react in polyvinyl alcohol solution, the degree of cross linking of the grade from which the solution becomes a gel is desirable. Moreover, the amount of the cross linking agent used to the monomeric unit of polyvinyl alcohol can adjust the degree of the bridge formation suitably.

[0020] Thus, in order to make the prepared polyvinyl alcohol bridge formation object into the separator for alkaline cells, it can carry out by the method of uniting with the network-structure object which fabricates this polyvinyl alcohol bridge formation object in configurations, such as the shape for example, of a sheet, or is mentioned later, and fabricating in configurations, such as the shape of a sheet, etc. In addition, in the aforementioned crosslinking reaction, since the polyvinyl alcohol bridge formation object acquired after crosslinking reaction has already become sheet-like when the method of sinking in sodium-tetraborate solution is used for the polyvinyl alcohol film prepared beforehand, even if it carries out, it is not necessary to perform fabrication of the addition made into the shape of a sheet.

[0021] Especially the method of fabricating the aforementioned polyvinyl alcohol bridge formation object in the shape of a sheet can use the method of drying on the glass plate which was not limited, for example, carried out Teflon processing, after carrying out a DIP coat, flow casting, a spin coat, and, and exfoliating, the method of casting on a direct zinc negative electrode, etc. As for

the thickness at the time of using the aforementioned polyvinyl alcohol bridge formation object as a sheet-like object, it is usually preferably desirable that it is 25-80 micrometers still more preferably 20-100 micrometers 10-200 micrometers.

[0022] The separator for alkaline cells of this invention may be the sheet-like object united with the network-structure object from the aforementioned polyvinyl alcohol bridge formation object that what is necessary is just substantial. Although any, such as textile fabrics, a nonwoven fabric, and a fine porous membrane, are sufficient as this network-structure object, especially its nonwoven fabric is desirable. Especially if the quality of the material is excellent in alkali resistance, it will not be limited, but polyolefines, such as polyethylene and polypropylene, a polysulfone, etc. can be used for it. Specifically, polyolefine system nonwoven fabric films, polysulfone system nonwoven fabrics, etc., such as polypropylene which performed hydrophilic processing, are mentioned. As for the thickness of these network-structure objects, it is usually preferably desirable that it is 0.2-1.0mm still more preferably 0.1-2.0mm 0.05-5.0mm. Since a network-structure object has the desirable one where ionic conductivity is higher, resistance of a network-structure object has an as much as possible desirable method of a low, and it is usually desirable that they are two or less ohm [ 50m] and cm preferably two or less 100m ohm-cm. Moreover, the thing of an electrolyte holding rate high as much as possible is desirable, and it is usually desirable that it is 200% or more still more preferably 100% or more. Resistance becomes high and is not desirable when an electrolyte holding rate is less than 100%.

[0023] Especially the manufacture method of the sheet-like object united with the aforementioned network-structure object can carry out the laminating of the bridge formation object after performing the method of not being limited, for example, making polyvinyl alcohol / sodium-tetraborate solution adhere by the method of flow casting, a spin coat, or a DIP coat on a nonwoven fabric as a suitable method, and drying, or polyvinyl alcohol crosslinking reaction to a network-structure object, and can mention the method of drying etc. The aforementioned laminating of only carrying out a laminating is even good, and can also be performed by the method of making both adhesives or a sheet-like object, and network-structure both [ one side or ] welding partially or on the whole etc. Moreover, although especially the aforementioned dryness is not limited, it can be carried out by the method usually dried on condition that 60-100 etc. degrees C etc. among room temperature neglect and a vacuum dryer overnight.

[0024] Since the separator for alkaline cells of this invention has the desirable one where ionic conductivity is higher, the membrane resistance has a desirable method of a low, and it is usually preferably desirable [ a membrane resistance ] that they are two or less ohm [ 150m] and cm still more preferably two or less 200m ohm-cm two or less 300m ohm-cm. The separator which has a low membrane resistance is obtained by optimizing the loadings and thickness of sodium tetraborate.

[0025] The alkaline cell of this invention is a primary cell or a rechargeable battery equipped with the aforementioned separator. In any case, it can be made into the well-known structure where a separator separates a negative electrode and a positive electrode, and let it be an alkaline cell. Especially the configuration of a cell may not be limited, any, such as a cylindrical shape, a square shape, and a button type, are sufficient as it, and any of an open sand mold or closed mold are sufficient as it.

[0026] Especially as the electrolytic solution of the aforementioned alkaline cell, although not limited, solution, such as KOH and NaOH, is mentioned. The concentration 5 - 50 % of the weight usually has 15 - 35 still more preferably desirable % of the weight ten to 40% of the weight preferably. Moreover, various inorganic ion can be added in the range which does not spoil the purpose of this invention.

[0027] As the aforementioned alkali primary cell, a zinc-2 manganese-oxide cell, a silver oxide cell, etc. are mentioned, for example. When producing a zinc-2 manganese-oxide cell using the separator of this invention, it is not necessary to add the mercury for suppressing a dendrite, and an environmental load can be made small into a zinc negative electrode.

[0028] Moreover, as the aforementioned alkali rechargeable battery, a nickel-zinc cell, a silver-zinc cell, a zinc-manganese cell, an air-zinc cell, a nickel hydride battery, etc. are mentioned, for example, and a nickel-zinc cell is especially desirable.

[0029] Although not limited, after applying conductors, such as carbon, to the sintering formula nickel and firing polyurethane which are mainly used with a nickel-cadmium battery especially as a nickel positive electrode of the aforementioned nickel-zinc rechargeable battery, the porosity nickel which carried out electroplating of the nickel and pyrolyzed polyurethane is mentioned. On the other hand, especially as a zinc negative electrode, although not limited, metallic oxides other than the material and the zinc oxide to which a zinc oxide and metal zinc were made to bind with a stable high molecular compound in the electrolytic solutions, such as a fluororesin, and metal zinc, such as indium oxide, are added, and the material to which it was made to bind with a high molecular compound is mentioned.

[0030] Since the aforementioned separator is excellent in dendrite-proof nature and electrolytic-solution retentivity, as for the produced rechargeable battery, power density becomes [ a cycle life ] long highly. Moreover, since elution of the metal from a hydrogen storage material can be suppressed in the case of a nickel hydride battery, a cycle life can be lengthened.

[0031]

[Effect of the Invention] The separator of this invention is excellent in electrolytic-solution-proof nature, dendrite-proof nature, and electrolytic-solution retentivity, and since ion conductivity is good, it is useful as a separator for alkaline cells. Moreover, the alkaline cell equipped with this separator has high stability, and especially an alkali rechargeable battery shows the outstanding cycle life etc.

[0032]

[Example] Although an example and the example of comparison explain to a detail further below, this invention is not limited to these.

[0033]

[Example 1] It was dropped heating 0.90ml (a borax being used) of sodium-tetraborate solution of concentration 4.8% of the

weight 2.5% of the weight in 60ml of polyvinyl alcohol (tradename "PVA-HC", Kuraray Co., Ltd. make, average-degree-of-polymerization 1750 and 1, and 2-diol joint content % of 1.5 mols) solution of concentration, and homogeneous polyvinyl alcohol / sodium-tetraborate solution were obtained. Then, this solution was cast on the 15cmx15cm glass substrate, and dryness hardening was carried out by room temperature neglect overnight. Furthermore the vacuum drying was performed and the film of 50 micrometers of thickness was obtained. The mole ratio of the sodium tetraborate to the monomeric unit of the polyvinyl alcohol of the obtained film was 300:1. The membrane-resistance value measured by the alternating current call RAUSHU method was the 148m ohm-cm 2.

[0034]

[Example 2] Except having set the amount of the sodium-tetraborate solution of concentration to 0.54ml 4.8% of the weight, it was the same conditions as an example 1, and after preparing polyvinyl alcohol / sodium-tetraborate solution, creation of a bridge formation body membrane was performed. The thickness of the obtained film was 52 micrometers. The mole ratio of the sodium tetraborate to the monomeric unit of the polyvinyl alcohol of the obtained film was 500:1. The membrane-resistance value measured by the alternating current call RAUSHU method was the 123m ohm-cm 2.

[0035]

[Example 3] The polyvinyl alcohol / sodium-tetraborate solution prepared like the example 1 were cast on the polypropylene fine porous membrane (a tradename "Celgard", Daicel Chemical Industries, Ltd. make) of 25 micrometers of thickness, and it was made to dry by room temperature neglect overnight. Furthermore the vacuum drying was performed and the cascade screen of 78 micrometers of thickness was obtained. The membrane-resistance value measured by the alternating current call RAUSHU method was the 195m ohm-cm 2.

[0036]

[Example 4] The polyvinyl alcohol / sodium-tetraborate solution prepared like the example 2 were cast on the polypropylene fine porous membrane (a tradename "Celgard", Daicel Chemical Industries, Ltd. make) of 25 micrometers of thickness, and it was made to dry by room temperature neglect overnight. Furthermore the vacuum drying was performed and the cascade screen of 78 micrometers of thickness was obtained. The membrane-resistance value measured by the alternating current call RAUSHU method was the 180m ohm-cm 2.

[0037]

[The example 1 of comparison] 60ml of polyvinyl alcohol (tradename "PVA-HC", Kuraray Co., Ltd. make, average-degree-of-polymerization 1750 and 1, and 2-diol joint content % of 1.5 mols) solution of concentration was cast on the 15cmx15cm glass substrate 2.5% of the weight, and dryness hardening was carried out by room temperature neglect overnight. The vacuum drying was performed after that and the film of 43 micrometers of thickness was obtained. The membrane-resistance value measured by the alternating current call RAUSHU method was the 131m ohm-cm 2.

[0038]

[The example 2 of comparison] 60ml of polyvinyl alcohol (tradename "PVA-HC", Kuraray Co., Ltd. make, average-degree-of-polymerization 1750 and 1, and 2-diol joint content % of 1.5 mols) solution of concentration was cast 2.5% of the weight on the 15cmx15cm polypropylene fine porous membrane of 25 micrometers of thickness, and dryness hardening was carried out by room temperature neglect overnight. The vacuum drying was performed after that and the cascade screen of 68 micrometers of thickness was obtained. The membrane-resistance value measured by the alternating current call RAUSHU method was the 182m ohm-cm 2.

[0039]

[Example 5] The nickel-zinc cell shown in drawing 1 using the separator produced in the examples 1-4 was created. The negative-electrode charge collector 2 with which the zinc negative-electrode active material 1 was carried out a roll pressure total, and the positive-electrode charge collector 7 with which the nickel positive active material 6 was sintered are held in the main part 9 of a container in the state where it was isolated by the separator 5 through \*\*\*\*\* (3 4), and this nickel-zinc cell is sealed with the container lid 9.

[0040] The aforementioned zinc negative-electrode active material 1 is the kneading object which kneaded ZnO:Zn:fluororesin dispersion =80:15:5 while adding water, and a nickel mesh was used for the negative-electrode charge collector 2. After rolling, this negative electrode has been arranged, after carrying out vacuum heating. On the other hand as a positive-electrode charge collector, a nickel mesh was used, using KARUBO nickel as a nickel positive active material. Since nickel (OH)<sub>2</sub> was infiltrated, this positive electrode has been arranged. It is used infiltrating this electrolytic solution into \*\*\*\*\* (3 4) and a separator 5 35% of the weight using the KOH solution of concentration as the electrolytic solution. In addition, when the separator created in the examples 3 and 4 is used, the polyvinyl alcohol side has been arranged to the zinc negative-electrode side. The theoretical cell capacity of the created cell was about 1.5 Ah(s).

[0041] The repeat charge and discharge of the created cell were carried out, respectively, and the cycle life was measured. The charge and discharge of a cell charged for 5 hours by 1/5C (quantity of electricity equivalent to geometric capacity is energized for 5 hours), and they discharged until the cell voltage was set to 1.0V by 1/4C, and when the cell capacity became 60% or less of the first stage, they were taken as the battery life. A result is shown in Table 1.

[0042]

[The example 3 of comparison] Except having used the separator created in the examples 1 and 2 of comparison, the nickel-zinc cell was created like the example 5 and the cycle life was measured. A result is shown in Table 1.

[0043]

[Table 1]

	サイクル寿命 (回)
実施例 1	2 1 0
実施例 2	1 5 0
実施例 3	3 5 0 以上
実施例 4	2 3 0
比較例 1	1 0
比較例 2	3 0

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**CLAIMS**

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[Claim(s)]

[Claim 1] The separator for alkaline cells which becomes substantial from the polyvinyl alcohol bridge formation object which constructed the bridge over the bottom of existence of a cross linking agent, and obtained polyvinyl alcohol, and is characterized by these cross linking agents being sodium tetraborate and/or a sodium-tetraborate hydrate.

[Claim 2] The separator for alkaline cells which it becomes substantial from the sheet-like object of the polyvinyl alcohol bridge formation object which constructed the bridge over the bottom of existence of a cross linking agent, and obtained polyvinyl alcohol, and these cross linking agents are sodium tetraborate and/or a sodium-tetraborate hydrate, and is characterized by uniting the aforementioned sheet-like object with a network-structure object.

[Claim 3] The alkaline cell equipped with the separator for alkaline cells according to claim 1 or 2.

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# PATENT ABSTRACTS OF JAPAN

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C08G 79/08  
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(71)Applicant : KONPON KENKYUSHO:KK  
TOYOTA MOTOR CORP

(22)Date of filing : 31.07.1997

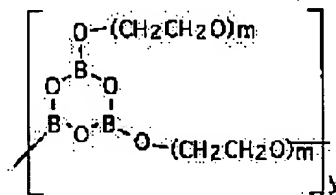
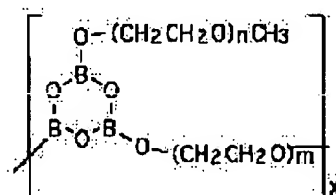
(72)Inventor : FUJINAMI TATSUO  
MARY AN MEHTA

## (54) BASE MATERIAL FOR ION CONDUCTOR AND ION CONDUCTOR

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance ion conductivity in a room temperature area on the basis of single ion conductivity by forming a base material as a structure that has an ion conductive molecule and boroxine rings which are bonded to the ion conductive molecule and capture an anion of ion conductive electrolyte salt.

SOLUTION: A base material for an ion conductor has plural boroxine rings, and is normally a soft solid. The boroxine rings attract an anion of electrolyte salt, and an ion conductive molecule takes charge of ion conductivity of a cation. The ion conductive molecule can be formed of a molecule having an ether chain. An ethyl ether chain and a propyl ether chain are desirable as the ether chain. To put it concretely, the ion conductive molecule is desirable to have a structure expressed by formula I and/or formula II. The base material for an ion conductor can be easily synthesized by adding boric oxide having tube prescribed mole number to a solution mixed with polyethylene glycol and polyethylene glycol monomethyl ether in a prescribed mixing ratio followed by heating.



II

## LEGAL STATUS

[Date of request for examination]

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[Detailed Description of the Invention]

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[Industrial Application] this invention relates to the alkaline cell which consists of an alkali primary cell and an alkali rechargeable battery equipped with the separator for alkaline cells, and this separator.

[0002]

[Description of the Prior Art] Conventionally, alkaline cells, such as a nickel-zinc cell, a nickel-cadmium battery, and a zinc-manganese cell, are equipped with the separator, in order to prevent the short circuit of a positive electrode and a negative electrode. Generally as a charge of separator material, the nonwoven fabric which consists of fiber, such as a polyamide, polypropylene, and a polysulfone, is used.

[0003] The aforementioned polyamide system nonwoven fabric has bad hot alkali resistance, since degradation by cutting of a chain takes place, while in use, a dendrite occurs and there is a trouble that a positive electrode and a negative electrode will short-circuit. Although excelled in alkali resistance, since the aforementioned polypropylene system nonwoven fabric is a hydrophobic property, its electrolytic-solution retentivity is bad. Therefore, if charge-and-discharge efficiency is bad and makes thickness thin, a leakage current will arise, and there is a trouble of it becoming impossible to use it as a cell. Although the electrolytic-solution retentivity of the aforementioned polysulfone system nonwoven fabric is good as compared with a polypropylene system nonwoven fabric, when thickness is made thin like a polypropylene system nonwoven fabric, a leakage current arises and there is a trouble of it becoming impossible to use it. further -- these nonwoven fabrics -- each -- fine -- since it has the hole, the actual condition cannot fully suppress a dendrite and especially generating of this dendrite is a critical defect in a zinc system alkaline cell

[0004] On the other hand, the laminating of the polyvinyl alcohol is carried out on a nonwoven fabric like a polypropylene nonwoven fabric, and the proposal (JP,3-1457,A) of creating a separator is made. However, there is a problem of the dendrite-proof nature of polyvinyl alcohol being inadequate, and causing degradation in the electrolytic solution.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is excellent in electrolytic-solution-proof nature, dendrite-proof nature, electrolytic-solution retentivity, etc., and is to offer the ion conductivity good separator for alkaline cells. Another purpose of this invention is to offer an alkaline cell with the high stability equipped with the separator which has the property which was excellent the account of before.

[0006]

[Means for Solving the Problem] According to this invention, it becomes substantial from the polyvinyl alcohol bridge formation object which constructed the bridge over the bottom of existence of a cross linking agent, and obtained polyvinyl alcohol, and the separator for alkaline cells characterized by these cross linking agents being sodium tetraborate and/or a sodium-tetraborate hydrate is offered. Moreover, according to this invention, it becomes substantial from the sheet-like object of the polyvinyl alcohol bridge formation object which constructed the bridge over the bottom of existence of a cross linking agent, and obtained polyvinyl alcohol, and the separator for alkaline cells which these cross linking agents are sodium tetraborate and/or a sodium-tetraborate hydrate, and is characterized by uniting the aforementioned sheet-like object with a network-structure object is offered. Furthermore by this invention, the alkaline cell equipped with these separators for alkaline cells is offered.

[0007] Hereafter, this invention is further explained to a detail. The separator for alkaline cells of this invention consists of substantially polyvinyl alcohol bridge formation objects which constructed the bridge in polyvinyl alcohol considering tetrapod boric-acid sodium and/or the tetrapod boric-acid sodium hydrate as a cross linking agent.

[0008] although especially the polyvinyl alcohol used by this invention is not limited -- average degree of polymerization 200-10000 -- it is preferably desirable 300-6000, and that it is 500-3000 still more preferably Since there is an inclination for the viscosity of polyvinyl alcohol solution to rise and for creation of a separator to become difficult when average degree of polymerization is less than 200, there is a possibility that dendrite-proof nature may fall and 10000 is exceeded, it is not desirable. Moreover, the degree of saponification has a desirable thing high as much as possible, and it is usually preferably desirable [ the degree ] that it is 97% or more still more preferably 90% or more 80% or more. The hydrophilic property of polyvinyl alcohol falls, so that the degree of saponification is low, and the electrolytic-solution maintenance nature of a separator becomes bad.

[0009] Although the aforementioned polyvinyl alcohol usually consists of 1 and 3-diol combination, 1 and 2-diol combination shown in the formula-ization 1 other than this combination as different-species combination may be contained.



out a DIP coat, flow casting, a spin coat, and, and exfoliating, the method of casting on a direct zinc negative electrode, etc. As for the thickness at the time of using the aforementioned polyvinyl alcohol bridge formation object as a sheet-like object, it is usually preferably desirable that it is 25-80 micrometers still more preferably 20-100 micrometers 10-200 micrometers.

[0022] The separator for alkaline cells of this invention may be the sheet-like object united with the network-structure object from the aforementioned polyvinyl alcohol bridge formation object that what is necessary is just substantial. Although any, such as textile fabrics, a nonwoven fabric, and a fine porous membrane, are sufficient as this network-structure object, especially its nonwoven fabric is desirable. Especially if the quality of the material is excellent in alkali resistance, it will not be limited, but polyolefines, such as polyethylene and polypropylene, a polysulfone, etc. can be used for it. Specifically, polyolefine system nonwoven fabric films, polysulfone system nonwoven fabrics, etc., such as polypropylene which performed hydrophilic processing, are mentioned. As for the thickness of these network-structure objects, it is usually preferably desirable that it is 0.2-1.0mm still more preferably 0.1-2.0mm 0.05-5.0mm. Since a network-structure object has the desirable one where ionic conductivity is higher, resistance of a network-structure object has an as much as possible desirable method of a low, and it is usually desirable that they are two or less ohm [ 50m] and cm preferably two or less 100m ohm-cm. Moreover, the thing of an electrolyte holding rate high as much as possible is desirable, and it is usually desirable that it is 200% or more still more preferably 100% or more. Resistance becomes high and is not desirable when an electrolyte holding rate is less than 100%.

[0023] Especially the manufacture method of the sheet-like object united with the aforementioned network-structure object can carry out the laminating of the bridge formation object after performing the method of not being limited, for example, making polyvinyl alcohol / sodium-tetraborate solution adhere by the method of flow casting, a spin coat, or a DIP coat on a nonwoven fabric as a suitable method, and drying, or polyvinyl alcohol crosslinking reaction to a network-structure object, and can mention the method of drying etc. The aforementioned laminating of only carrying out a laminating is even good, and can also be performed by the method of making both adhesives or a sheet-like object, and network-structure both [ one side or ] welding partially or on the whole etc. Moreover, although especially the aforementioned dryness is not limited, it can be carried out by the method usually dried on condition that 60-100 etc. degrees C etc. among room temperature neglect and a vacuum dryer overnight.

[0024] Since the separator for alkaline cells of this invention has the desirable one where ionic conductivity is higher, the membrane resistance has a desirable method of a low, and it is usually preferably desirable [ a membrane resistance ] that they are two or less ohm [ 150m] and cm still more preferably two or less 200m ohm-cm two or less 300m ohm-cm. The separator which has a low membrane resistance is obtained by optimizing the loadings and thickness of sodium tetraborate.

[0025] The alkaline cell of this invention is a primary cell or a rechargeable battery equipped with the aforementioned separator. In any case, it can be made into the well-known structure where a separator separates a negative electrode and a positive electrode, and let it be an alkaline cell. Especially the configuration of a cell may not be limited, any, such as a cylindrical shape, a square shape, and a button type, are sufficient as it, and any of an open sand mold or closed mold are sufficient as it.

[0026] Especially as the electrolytic solution of the aforementioned alkaline cell, although not limited, solution, such as KOH and NaOH, is mentioned. The concentration 5 - 50 % of the weight usually has 15 - 35 still more preferably desirable % of the weight ten to 40% of the weight preferably. Moreover, various inorganic ion can be added in the range which does not spoil the purpose of this invention.

[0027] As the aforementioned alkali primary cell, a zinc-2 manganese-oxide cell, a silver oxide cell, etc. are mentioned, for example. When producing a zinc-2 manganese-oxide cell using the separator of this invention, it is not necessary to add the mercury for suppressing a dendrite, and an environmental load can be made small into a zinc negative electrode.

[0028] Moreover, as the aforementioned alkali rechargeable battery, a nickel-zinc cell, a silver-zinc cell, a zinc-manganese cell, an air-zinc cell, a nickel hydride battery, etc. are mentioned, for example, and a nickel-zinc cell is especially desirable.

[0029] Although not limited, after applying conductors, such as carbon, to the sintering formula nickel and firing polyurethane which are mainly used with a nickel-cadmium battery especially as a nickel positive electrode of the aforementioned nickel-zinc rechargeable battery, the porosity nickel which carried out electroplating of the nickel and pyrolyzed polyurethane is mentioned. On the other hand, especially as a zinc negative electrode, although not limited, metallic oxides other than the material and the zinc oxide to which a zinc oxide and metal zinc were made to bind with a stable high molecular compound in the electrolytic solutions, such as a fluororesin, and metal zinc, such as indium oxide, are added, and the material to which it was made to bind with a high molecular compound is mentioned.

[0030] Since the aforementioned separator is excellent in dendrite-proof nature and electrolytic-solution retentivity, as for the produced rechargeable battery, power density becomes [ a cycle life ] long highly. Moreover, since elution of the metal from a hydrogen storage material can be suppressed in the case of a nickel hydride battery, a cycle life can be lengthened.

[0031]

[Effect of the Invention] The separator of this invention is excellent in electrolytic-solution-proof nature, dendrite-proof nature, and electrolytic-solution retentivity, and since ion conductivity is good, it is useful as a separator for alkaline cells. Moreover, the alkaline cell equipped with this separator has high stability, and especially an alkali rechargeable battery shows the outstanding cycle life etc.

[0032]

[Example] Although an example and the example of comparison explain to a detail further below, this invention is not limited to these.

[0033]

[Example 1] It was dropped heating 0.90ml (a borax being used) of sodium-tetraborate solution of concentration 4.8% of the weight 2.5% of the weight in 60ml of polyvinyl alcohol (tradename "PVA-HC", Kuraray Co., Ltd. make, average-degree-of-polymerization 1750 and 1, and 2-diol joint content % of 1.5 mols) solution of concentration, and homogeneous polyvinyl alcohol / sodium-tetraborate solution were obtained. Then, this solution was cast on the 15cmx15cm glass substrate, and dryness hardening was carried out by room temperature neglect overnight. Furthermore the vacuum drying was performed and the film of 50 micrometers of thickness was obtained. The mole ratio of the sodium tetraborate to the monomeric unit of the polyvinyl alcohol of the obtained film was 300:1. The membrane-resistance value measured by the alternating current call RAUSHU method was the 148m ohm-cm 2.

[0034]

[Example 2] Except having set the amount of the sodium-tetraborate solution of concentration to 0.54ml 4.8% of the weight, it was the same conditions as an example 1, and after preparing polyvinyl alcohol / sodium-tetraborate solution, creation of a bridge formation body membrane was performed. The thickness of the obtained film was 52 micrometers. The mole ratio of the sodium tetraborate to the monomeric unit of the polyvinyl alcohol of the obtained film was 500:1. The membrane-resistance value measured by the alternating current call RAUSHU method was the 123m ohm-cm 2.

[0035]

[Example 3] The polyvinyl alcohol / sodium-tetraborate solution prepared like the example 1 were cast on the polypropylene fine porous membrane (a tradename "Celgard", Daicel Chemical Industries, Ltd. make) of 25 micrometers of thickness, and it was made to dry by room temperature neglect overnight. Furthermore the vacuum drying was performed and the cascade screen of 78 micrometers of thickness was obtained. The membrane-resistance value measured by the alternating current call RAUSHU method was the 195m ohm-cm 2.

[0036]

[Example 4] The polyvinyl alcohol / tetrapod boric-acid sodium solution prepared like the example 2 were cast on the polypropylene fine porous membrane (a tradename "Celgard", Daicel Chemical Industries, Ltd. make) of 25 micrometers of thickness, and it was made to dry by room temperature neglect overnight. Furthermore the vacuum drying was performed and the cascade screen of 78 micrometers of thickness was obtained. The membrane-resistance value measured by the alternating current call RAUSHU method was the 180m ohm-cm 2.

[0037]

[The example 1 of comparison] 60ml of polyvinyl alcohol (tradename "PVA-HC", Kuraray Co., Ltd. make, average-degree-of-polymerization 1750 and 1, and 2-diol joint content % of 1.5 mols) solution of concentration was cast on the 15cmx15cm glass substrate 2.5% of the weight, and dryness hardening was carried out by room temperature neglect overnight. The vacuum drying was performed after that and the film of 43 micrometers of thickness was obtained. The membrane-resistance value measured by the alternating current call RAUSHU method was the 131m ohm-cm 2.

[0038]

[The example 2 of comparison] 60ml of polyvinyl alcohol (tradename "PVA-HC", Kuraray Co., Ltd. make, average-degree-of-polymerization 1750 and 1, and 2-diol joint content % of 1.5 mols) solution of concentration was cast 2.5% of the weight on the 15cmx15cm polypropylene fine porous membrane of 25 micrometers of thickness, and dryness hardening was carried out by room temperature neglect overnight. The vacuum drying was performed after that and the cascade screen of 68 micrometers of thickness was obtained. The membrane-resistance value measured by the alternating current call RAUSHU method was the 182m ohm-cm 2.

[0039]

[Example 5] The nickel-zinc cell shown in drawing 1 using the separator produced in the examples 1-4 was created. The negative-electrode charge collector 2 with which the zinc negative-electrode active material 1 was carried out a roll pressure total, and the positive-electrode charge collector 7 with which the nickel positive active material 6 was sintered are held in the main part 9 of a container in the state where it was isolated by the separator 5 through \*\*\*\*\* (3 4), and this nickel-zinc cell is sealed with the container lid 9.

[0040] The aforementioned zinc negative-electrode active material 1 is the kneading object which kneaded ZnO:Zn:fluororesin dispersion =80:15:5 while adding water, and a nickel mesh was used for the negative-electrode charge collector 2. After rolling, this negative electrode has been arranged, after carrying out vacuum heating. On the other hand as a positive-electrode charge collector, a nickel mesh was used, using KARUBO nickel as a nickel positive active material. Since nickel (OH)<sub>2</sub> was infiltrated, this positive electrode has been arranged. It is used infiltrating this electrolytic solution into \*\*\*\*\* (3 4) and a separator 5 35% of the weight using the KOH solution of concentration as the electrolytic solution. In addition, when the separator created in the examples 3 and 4 is used, the polyvinyl alcohol side has been arranged to the zinc negative-electrode side. The theoretical cell capacity of the created cell was about 1.5 Ah(s).

[0041] The repeat charge and discharge of the created cell were carried out, respectively, and the cycle life was measured. The charge and discharge of a cell charged for 5 hours by 1/5C (quantity of electricity equivalent to geometric capacity is energized for 5 hours), and they discharged until the cell voltage was set to 1.0V by 1/4C, and when the cell capacity became 60% or less of the first stage, they were taken as the battery life. A result is shown in Table 1.

[0042]

[The example 3 of comparison] Except having used the separator created in the examples 1 and 2 of comparison, the nickel-zinc cell was created like the example 5 and the cycle life was measured. A result is shown in Table 1.

[0043]

[Table 1]

	サイクル寿命 (回)
実施例 1	2 1 0
実施例 2	1 5 0
実施例 3	3 5 0 以上
実施例 4	2 3 0
比較例 1	1 0
比較例 2	3 0

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[Translation done.]

**\* NOTICES \***

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The separator for alkaline cells which becomes substantial from the polyvinyl alcohol bridge formation object which constructed the bridge over the bottom of existence of a cross linking agent, and obtained polyvinyl alcohol, and is characterized by these cross linking agents being sodium tetraborate and/or a sodium-tetraborate hydrate.

[Claim 2] The separator for alkaline cells which it becomes substantial from the sheet-like object of the polyvinyl alcohol bridge formation object which constructed the bridge over the bottom of existence of a cross linking agent, and obtained polyvinyl alcohol, and these cross linking agents are sodium tetraborate and/or a sodium-tetraborate hydrate, and is characterized by uniting the aforementioned sheet-like object with a network-structure object.

[Claim 3] The alkaline cell equipped with the separator for alkaline cells according to claim 1 or 2.

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[Translation done.]